Studies on the Production of Tantalum by Electrolysis of Fused Salt. II : On the Ionic Form and the Equilibrium of the Fused Salt

Studies on the Production of Tantalum by Electrolysis of Fused Salt. II On the Ionic Form and the Equilibrium of the Fused Salt*

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Synopsis

The alkali sides of the binary phase diagrams, KF-K_2TaF_7, KCl-K_2TaF_7, KBr-K_2TaF_7, KF-KCl·K_2TaF_7, KBr-KF·K_2TaF_7, and NaCl-K_2TaF_7 were made for the purpose of investigating the ionic form of the components in the electrolytic fused bath. Assuming that all the phase diagrams were simple eutectic systems and each ionic activity coefficient was unity, the equation of the freezing point depression was applied to the liquidus curves of the alkali sides as follows :

$$T = \frac{T_0}{1 - \frac{\Delta H}{R} \ln a_A},$$

where the activity of the component A, a_A, is $\gamma_A \prod_i N_+^{\nu_i^+} \prod_j N_-^{\nu_j^-}$, and N^+ and N^- represent Temkin's ionic mole fractions. From the agreement of the measured values with the theoretical, the complex ionic equilibria were deduced as follows :

$$TaF_7^{--} + F^- = TaF_8^{---},$$

$$TaF_7^{--} + Cl = TaF_7Cl^{---},$$

and the relation between equilibrium constants K_1 and K_2 was represented by $K_1 > K_2$.

I. Introduction

In the production of tantalum by the fused salt electrolysis, the system containing potassium tantalum fluoride and alkali halides was employed as a solvent of tantalum oxide. In the previous work(1), it was found that the phase diagrams of two solvent systems of the oxide, KF-K_2TaF_7 and KCl-K_2TaF_7, formed the eutectics. In addition, the alkali halide sides were studied from the viewpoint of experimental accuracy and purity of usable reagents, by selecting four binary solvent systems containing no tantalum oxide. The equation of freezing point depression using Temkin's ionic mole fractions was applied to the liquidus curves on the alkali halide sides of the diagrams, assuming that they all formed the eutectics that the ionic activity coefficient was unity : and thus the ionic form in the fused state was deduced.

Although several studies have already been made of the mechanism of

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(1) T. Iuchi and K. Ono, Sci. Rep. RITU, A **13** (1961), 456.

electrolytic deposition of tantalum[2][3], it is difficult to analyze measured values theoretically, because few studies have been made of the fundamental system of the electrode reaction, and the system is complicated in the practical electrolysis. And owing to experimental difficulty encountered in the fluoride melt at high temperature and to poor fundamental knowledge on the fused slat, the mechanism has not yet been completely interpreted.

The theoretical ground utilized in this report is next described. On the liquidus curve of eutectic phase diagram having no solid solution, the pure component A in the solid phase was in equilibrium with A in the molten mixture as follows:

$$\text{A (pure solid)} \rightleftharpoons \text{A (molten mixture)} . \tag{1}$$

In the above equilibrium, equation (2) is held among the activity of the component A, a_A, the temperature T, and the pressure P.

$$d \ln a_A = \frac{\Delta H}{R} \frac{dT}{T^2} - \frac{\Delta V}{R} \frac{dP}{T} \tag{2}$$

where R is the gas constant, ΔH the difference in the molar enthalpies between the liquid state and the solid, and ΔV the difference in the molar volumes between the liquid state and the solid. Although ΔH depends on L, it can be regarded as constant over a small temperature range. The 2nd term is generally negligible. By integration of equation (2) from T_0 to T under the above conditions and by solving it with respect to T, the following equation was obtained:

$$T = \frac{T_0}{1 - \frac{\Delta H}{R} \ln \frac{a_A(T)}{a_A(T_0)}} , \tag{3}$$

where $a_A\ (T_0)$ was taken as unity.

Fused salts in general belong to the strong electrolytes. The component A in the fused state exists in various ionic forms and not in molecular one. Accordingly it is now assumed that the component A dissociates into ν_i moles of positive ion B^+ and ν_z moles of negative C^- as follows:

$$A = \sum_i \nu_i B^+ + \sum_j \nu_j C^- .$$

In this case the activity a_A is given by the following equation:

$$a_A = r_A \prod_i N^{\nu i}{}_+ \prod_j N_-{}^{\nu j}{}_- , \tag{4}$$

where γ_A is the ionic activity coefficient and N_+ or N_- the ionic mole fraction of the positive or the negative ion respectively. There are three kinds of ionic mole fraction; Herashimenko's, Temkin's and of solid solution. Temkin's ionic mole fraction is reported to be suitable for experimental interpretation of melts[4] (Herashimenko's is applied well to the ion of gas and that of solid solution to

(2) P. Drossbach, Z. Elektrochem., **57** (1953), 555.
(3) P. Drossbach and P. Petrick, Z. Elektrochem., **61** (1957), 410.

mixed ionic crystal). In the present work, the experimental results are analyzed by Temkin's ionic mole fraction as follows:

$$N_+ = \frac{n_i^+}{\sum_i n_i^+} \qquad N_- = \frac{n_j^-}{\sum_j n_j^-} ,$$

where n is the mole number of the ion.

In case of comparison of measured values with the theoretical, both must be discussed within the limit of the errors of the both and therefore this problem was studied.

For example, the error of temperature was calculated in the case of $N_{KCl} = 0.9$ in the system NaCl-K_2TaF_7 by assuming K^+, Cl^-, and TaF_7^{--}. Applying this assumption to equation (3) and making the calculation stated later, the following equation was obtained:

$$T = \frac{T_0}{1 - \frac{\Delta H}{R} \ln N_{KCl}} .$$

As the temperature error $|\Delta T|$ depends on ΔH and M_{KCl}, the equation of error can be given as follows:

$$|\Delta T| \leqq \frac{T_0}{R} \left(1 - \frac{\Delta H}{R} \ln N_{KCl}\right)^{-2} \left\{1 \ln N_{KCl} \Delta(\Delta H)| + |\Delta H \frac{\Delta N_{KCl}}{N_{KCl}}|\right\} ,$$

where T_0 is the melting point of potassium chloride, namely, 1043°K. According to Kwbaschewski, ΔH is $-6.1 + 0.3$ Kcal/mol. and therefore, $\Delta(\Delta H)$ is 0.3 Kcal/mol. The composition error ΔN_{KCl} is believed to be within $\pm$ 1 per cent and so ΔN_{KCl} is 0.001. When each value is introduced into the equation of error, ΔT is ± 0.5°C. This is within the experimental error ± 1°C and therefore, the comparison can be made between the measured values and the theoretical.

II. Experimental procedure

The specimen and the experimental method are the same as those used in the previous work[1].

III. Experimental results and considerations

The alkali sides of the phase diagrams were studied in this work because of the problem of the purity of potassium tantalum fluoride and the limitation in the apparatus. It was assumed that the alkali halides would dissociate completely as follows:

$$KF\ (Cl, Br) = K^+ + F^-\ (Cl^-, Br^-), \qquad (5)$$

$$NaCl = Na^+ + Cl^-. \qquad (5')$$

Hence, V_i and V_j are unity. As the concentration discussed was confined to

(4) H. Flood, T. Förland and B. Roald, J. Amer. Chem. Soc., **71** (1949), 572.

dilute solution of potassium tantalum fluoride, it was assumed that γ_A was unity and that the solvent and the solute would dissociate completely. Accordingly, the activity of alkali halide was represented as follows:

$$A_A = N_+ \cdot N_- .$$

Measurements were made to 0.15 of the mole fraction of the solute, that is, within the limit of dilute solution.

Various dissociations can be considered for those of potassium tantalum fluoride. In the first place, the dissociation in aqueous solution may be represented by the following equation:

$$K_2TaF_7 = K^+ + KTaF_7^{--} = 2K^+ + TaF_7^{--} . \quad (6)$$

As a melt has properties like a solid and the temperature discussed is in the vicinity of the melting point, considerations can be made from the standpoint of solid theory. It is natural that the following dissociations can be postulated because the complexes, $KTaF_6$, K_2TaF_7, and K_3TaF_8 in the system $KF\text{-}TaF_5$ are known.

$$K_2TaF_7 = 2K^+ + TaF_6^- + F^- , \quad (7)$$

$$K_2TaF_7 = 2K^+ + TaF_7^{--} , \quad (8)$$

$$KF \cdot K_2TaF_7 = 3K^+ + TaF_8^{---} , \quad (9)$$

$$KCl \cdot K_2TaF_7 = 3K^+ + TaF_7Cl^{---} . \quad (10)$$

Here attention must be paied to the dissociation number of K^+ as discussed later. In spite of the high concentration of K^+ in the melt, its ion has little effect on the dissociation of anions as shown later. ΔH is adopted from the book of Kubaschewski et al.[5] The melting points of the alkali halides used in our calculation agree with those in the book within $\pm 1°C$ and the calculations were made by using the present observed values.

Each system is first discussed and then all the systems are summarized.

1) The systems $KCl\text{-}K_2TaF_7$ and $NaCl\text{-}K_2TaF_7$

Assuming that the system $KCl\text{-}K_2TaF_7$ is composed of (5) and (7),

$$a_{KCl} = N_{K+} \cdot N_{Cl-} ,$$

$$N_{K+} = 1, \quad N_{Cl-} = \frac{n_{Cl-}}{n_{Cl-} + n_{TaF_6-} + n_{F-}} .$$

Also $n_{Cl-} = n_{KCl}$, $n_{TaF_6-} = n_{K_2TaF_7}$, $n_{F-} = n_{K_2TaF_7}$. $N_{K_2TaF_7} = n_{K_2TaF_7}/n_{KCl} + n_{K_2TaF_7}$ and $N_{KCl} = n_{KCl}/n_{KCl} + n_{K_2TaF_7}$ when $N_{KCl} + N_{K_2TaF_7} = 1$ and then

$$a_{KCl} = \frac{N_{KCl}}{2 - N_{KCl}} .$$

In the above equation, -6,100 for ΔH and 1,043 for T_0 are introduced into equation (3) and the freezing point depression curve is obtained as the lowest curve

(5) O. Kubaschewski and E.L.L. Evans, *Metallurgical Thermochemistry*, (1958), 296.

in Fig. 1, which does not agree with the measured values. According to the above method, the two dotted lines are obtained as shown in Fig. 1, when (5) is combined with (8) or with (10).

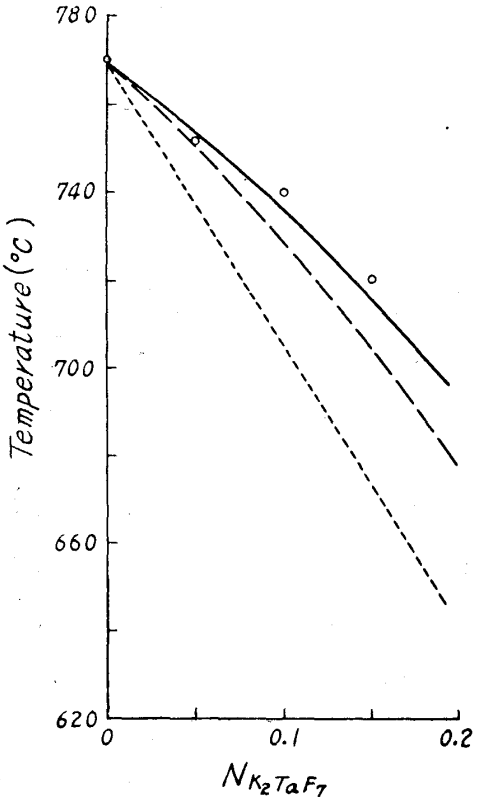

Fig. 1. The system KCl-K_2TaF_7.
..... K^+, Cl^-, TaF_6^-
——— K^+, Cl^-, TaF_7^{--}
— — K^+, Cl^-, TaF_7Cl^{---}
○ This work

The measured values stand in the curve from the assumption that the system is composed of K^+, Cl^- and TaF_7^{--}. This curve corresponds to both dissociations of (6) becouse we use Temkin's ionic mole fraction. Therefore it is impossible to know whether potassium tantalum fluoride produces one or two potassium ions because NK^+ is unity. In order to solve this problem, a measurement was made at the point of $N_{KCl}=0.9$ in the system NaCl-K_2TaF_7.

When (5) was combined with the 1st dissociation of (6), A_{NaCl} was N^2_{NaCl}, but a_{NaCl} was $N^2_{NaCl}/2\text{-}N_{NaCl}$ when (5) was combined with the 2nd dissociation of (6). The measured values agreed with the latter. Although the melting point of KCl is different from that of NaCl, both are the crystals of face-centered lattice and similar in the chemical properties. Therefore in the system KCl-K_2TaF_7, potassium tantalum fluoride is considered to produce two potassium ions. This agrees with the symmetric position of potassium ion in the crystal. From the above results, it is considered that the system KCl-K_2TaF_7 is composed of K^+, Cl^-, and TaF_7^{--}.

2) The system KBr-K_2TaF_7

In the above system, evaporation of the fluoride is so strong that the measurement is difficult. So the measurement was made of the system KBr-K_2TaF_7, as potassium bromide is similar to potassium chloride in chemical properties and has lower melting point. The measured values and the theoretical are shown in Fig. 2. The result similar to the above was obtained : it is considered that this system is composed of K^+, Br^-, and TaF_7^{--}.

3) The system KF-K_2TaF_7

On an assumption that (5) is combined with (7), (8) and (9), the theoretical curves shown in Fig. 3 were obtained. The measured values agreed with the large

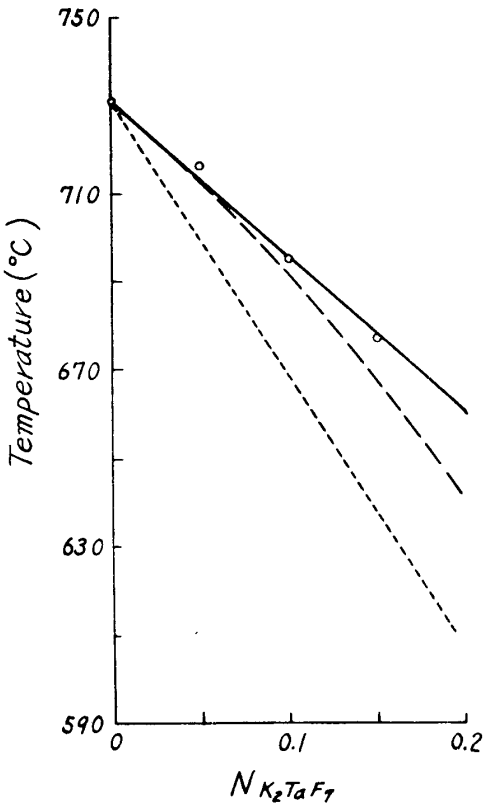

Fig. 2. The system KBr-K_2TaF_7.
..... K^+, Br^-, TaF_6^-
——— K^+, Br^-, TaF_7^{--}
— — K^+, Br^-, TaF_7Br^{---}
○ This work

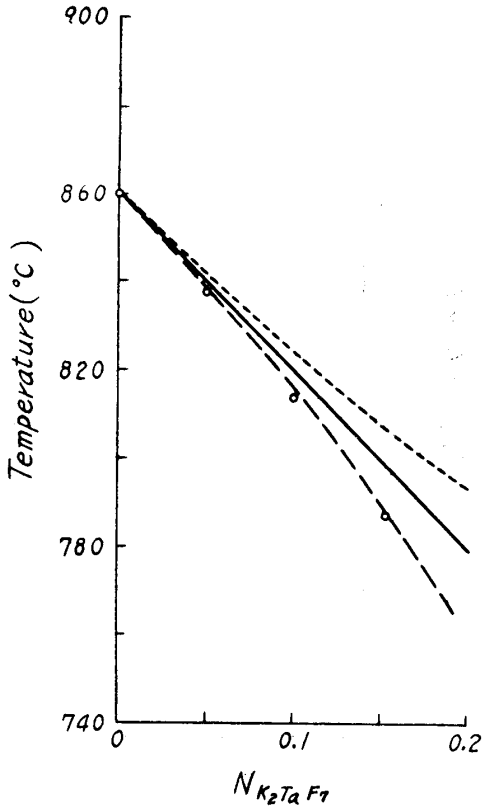

Fig. 3. The system KF-K_2TaF_7.
..... K^+, F^-, TaF_6^-
——— K^+, F^-, TaF_7^{--}
— — K^+, F^-, TaF_8^{---}
○ This work

dotted line, which means the consistence of K^+, F^- and TaF_8^{---}. From this figure, the following reaction is considered to form TaF_8^{---}

$$KF + K_2TaF_7 = 3K^+ + TaF_8^{---}.$$

This point will be described later.

4) The system KBr-KF.K_2TaF_7

Potassium bromide is not used as a component of the electrolytic bath. Because potassium chloride has a high melting point and because strong evaporation lowers the experimental accuracy, potassium bromide is used in the place of potassium chloride. It is considered that the results from the potassium bromide system hold true of the potassium chloride system. The theoretical curves of the combinations of (5) with (8) or (9) are shown in Fig. 4. The measured values stand in the curve of TaF_7^{---} but not in that of TaF_8^{---}. This agreement may be attributed to the following reason: This system is dilute with respect to potassium tantalum fluoride. Even if TaF_8^{---} is formed, it is apt to dissociate and therefore it is expected that there is an equilibrium between TaF_8^{---} and TaF_7^{--} as follows:

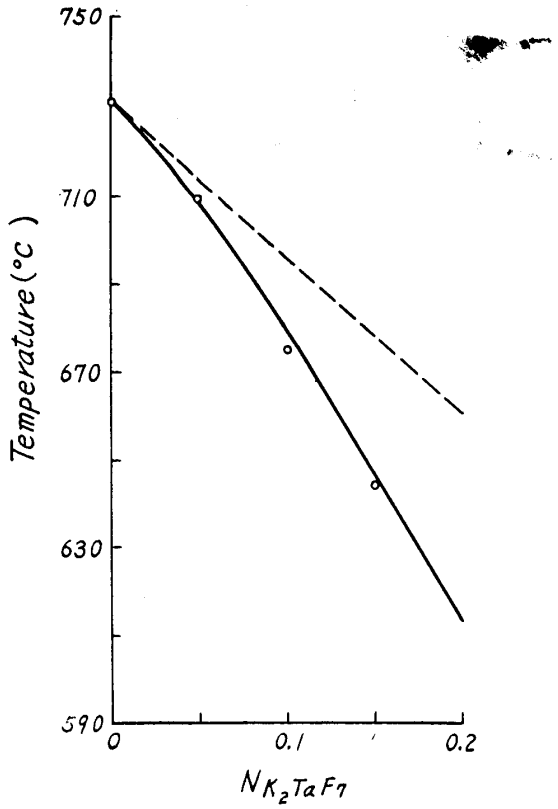

Fig. 4. The system KBr-K_2TaF_7.
——— K^+, Br^-, F^-, TaF_7^{--}
— — — K^+, Br^-, TaF_8^{---}
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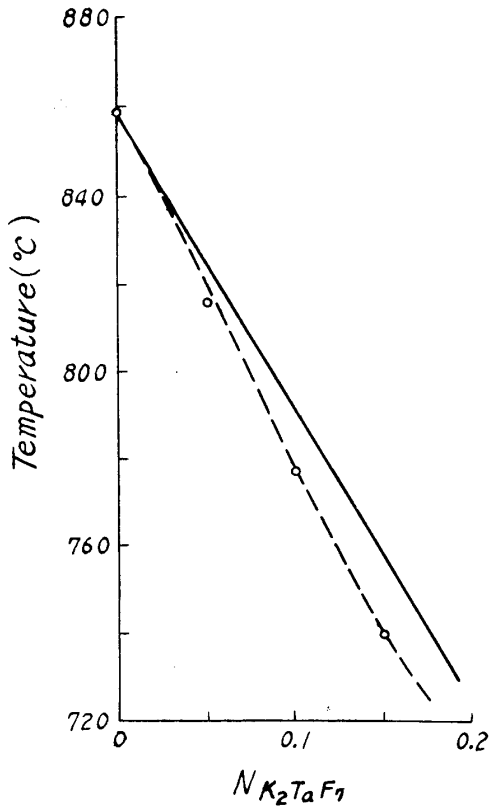

Fig. 5. The system KF-KCl·K_2TaF_7.
——— K^+, F^-, Cl^-, TaF_7^{--}
— — — K^+, F^-, Cl^-, TaF_8^{---}
○ This work

$$TaF_7^{--} + F^- = TaF_8^{---}. \qquad (11)$$

The equilibrium constant K_1 is obtained from (11) as follows:

$$K_1 = \frac{[TaF_8^{---}]}{[TaF_7^{--}]\,[F^-]},$$

where the brackets show the activities of the ionic species.

5) The system FK-KCl·K_2TaF_7.

As stated in the previous work, the system FK-KCl·K_2TaF_7 has an excellent ability as the solvent of tantalum oxide. It is better to work with lower concentration of potassium fluoride in practical electrolysis than that of this system. The system in which potassium bromide is replaced with potassium fluoride has the same composition as that of the practical bath. The system containing potassium fluoride, potassium chloride and potassium tantalum fluoride is of interest in the study of electrolysis.

The measured values and the theoretical curves of the combinations of (5) with (8) or with (10) are shown in Fig. 5. It shows that the system is composed of K^+, F^-, Cl^-, and TaF_8. This conclusion can be attributed to the following reason.

For the equilibrium

$$TaF_7^{--} + Cl^- = TaF_7Cl^{---}. \quad (12)$$

It follows from that

$$K_2 = \frac{[TaF_7Cl^{---}]}{[TaF_7^{--}]\,[Cl^-]}.$$

No curve in Figs. 1 to 5 agrees with that of TaF_7Cl^{---}. The system KCl-K_2TaF_7 can be expected to be the system in which Ta_7FCl^{---} has a direct effect on the depression of the freezing point, but it is not so. It seems that TaF_7Cl^{---} does not exist, but assuming a small equilibrium constant K_2, it gives a small formation of TaF_7Cl^{---}. It seems natural that TaF_7^{--} has a direct effect on the change of the activity in the system KCl-K_2TaF_7. Also in this system, in the case of a small K_2 and therefore, when it is diluted with respect to KCl·K_2TaF_7, the reactions proceeds to the left side. But TaF_7^{--} is formed, as the coexisted F^- is in equilibrium with TaF_7^{--} formed by (12) when $K_1 > K_2$, By comparing the ionic radii of F^- and Cl^-, as shown in Table 1, the quantitative agreement with the

Table 1. Ionic radii (Å).

ion	F^-	Cl^-	Br^-
ionic radius	1.36	1.81	1.95

assumption $K_1 > K_2$ is considered. F^- can combine more strongly with tantalum than with Cl^- and TaF_8^{---} will be stable at high temperature followed by violent thermal movements. From the above results, the following reaction proceeds:

$$TaF_7Cl^{---} + F^- = TaF_8^{---} + Cl^-$$

As stated in the previous work, the evaporated amount is smaller in the system KF-K_2TaF_7 than that in the system KCl-K_2TaF_7, although the temperature is higher. This agrees with the relation $K_1 > K_2$. The addition of potassium-tantalum fluoride drives the equilibrium to the right side to form TaF_8^{---} and controls the change of the composition by evaporation. Drossbach does not recommend the use of potassium fluoride from the results of electrolysis, but it is believed that a small quantity of potassium fluoride is worth employing as a com ponent of the electrolytic bath because of the above excellent properties and the solving abilities of tantalum oxide as stated in the previous report.

Summary

The equilibria $TaF_7^{--} + F^- = TaF_8^{---}$ and $TaF_7^{--} + Cl^- = TaF_7Cl^{---}$ and the relation of the equilibrium constant $K_1 > K_2$ were presumed on the liquidus curves of the alkali sides of the phase diagrams K_2TaF_7– alkali halides.